

Method of achieving a shape-memory effect on hair

The present invention concerns a method of providing a recallable hair shape transformation using active agents, which 5 provide hair with a shape-memory effect, in particular macromers which are cross-linkable to shape memory polymers or shape memory polymers.

In the field of shaping of hair, a distinction is usually made 10 between temporary hair-shaping methods and long-lasting, permanent hair-shaping methods. A temporary hair-shaping usually occurs in connection with the use of compositions on the basis of solutions or dispersions comprising hair-fixative polymers. Such products provide the hair, by means of the 15 polymers used, with improved hold, volume, elasticity, body and shine. Such styling products facilitate, for example, in the form of a gel, the shaping and provision of a hairdo; they improve, in the form of hair spray, the condition of a prepared hairdo; and they increase, in the form of setting foams, the 20 volume of the hair. A drawback in this connection is that the desired effects are of only relatively short duration, and that they are lost under external influences, such as combing, wind, high humidity, or contact with water. A permanent hair transformation usually occurs during a treatment of providing a 25 permanent wave. During this treatment the disulfide bonds in the hair are cleaved by use of a reductive reaction, the hair is brought into the new shape, and this new shape is fixed by

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providing new disulfide bonds by means of an oxidative process.

A drawback in this respect, however, is that the required chemical treatment of the hair employing reduction agents and oxidation agents involves an impairment of the structure of the

5 hair. A further drawback of the methods for hair shaping known up to now is that it is not possible to revert a once-performed transformation (shaping) using relatively simple means, i.e., it is not possible to change from one shape of a hairdo to another shape of a hairdo without troublesome processes.

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JP 04-41416 discloses compositions in the field of cosmetic preparations for hair which comprise specific linear polyurethanes having a glass transition temperature  $T_g$  of from 40 to 90°C. The process for hair treatment disclosed therein 15 corresponds to the treatment using conventional thermoplastic materials. After the administration of the composition, a hairdo is prepared at a temperature above  $T_g$ , and this hairdo is then fixed by means of cooling under  $T_g$ . During a subsequent rewarming to a temperature above  $T_g$ , the polymer softens and a 20 new hairdo can be prepared. A method for a recallable, reversible hair-shaping (hair transformation), however, is not disclosed. The properties of the linear polyurethanes are not satisfactory in order to provide a recallable hair shaping.

25 The object underlying the present invention was to provide a method and the therefore required products for providing a

recallable hair transformation (hair-shaping) enabling a high degree of recovery of a once-programmed hairdo. A further object was to provide a method enabling a permanent hair-shaping without requiring an impairing intervention into the

5 hair structure. A further object was the provision of a method which enables the reversion of a temporary transformation/shaping over multiple cycles with a high accuracy in order to revert to a previously prepared, programmed permanent hairdo. A further object was also the

10 provision of a method which enables in a simple manner to remedy with a high accuracy the deformation of a hairdo which has been introduced by external influences, in order to revert to a once prepared, programmed permanent hairdo.

15 This object has been solved with a method for treating hair, comprising:

applying onto the hair a composition which comprises at least one active agent, select among compounds which, alone or in

20 combination with further compounds, is capable, after application to hair and after having carried out the treatment defined in the following, to provide a shape memory effect to hairs,

25 previously, at the same time or subsequently bringing the hair into a desired shape (permanent memory shape), and

subsequently fixing the memory shape by inducing a physical or chemical change of the applied active agents,

wherein after a desired or undesired deformation of the memory

5 shape the initial memory shape can be recovered substantially by means of a physical stimulation.

A preferred embodiment concerns a method for hair treatment, comprising the steps of

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applying a composition, which comprises at least one crosslinkable macromer, which forms after crosslinking a shape-memory polymer, onto the hair, wherein the macromer

15 a. comprises crosslinkable areas (segments) which are crosslinkable by means of chemical bonds and

b. thermoplastic areas (segments) which are not chemically crosslinkable,

- bringing the hair, previously, at the same time or

20 subsequently, into a desired (permanent) shape and

- fixing the shape by means of chemical crosslinking of the macromer, thereby providing the shape memory polymer,

characterized in that the shape memory polymer possesses at

25 least one transition temperature  $T_{trans}$ .

A further object of the present invention is a method for impressing a second hairdo over a programmed, recallable first hairdo. In this method, a hairdo, programmed by means of the above-explained method (permanent shape) is heated to a 5 temperature above  $T_{trans}$ . Subsequently, the hair is brought into the second (temporary) shape and the second shape is fixed by means of cooling to a temperature below  $T_{trans}$ .

A further subject of the present invention is a method for the 10 recovery of a first hairdo, programmed by means of the above-explained method (permanent shape). Therein, a hairdo in a temporary shape or in the shape of a hairdo obtained by means of cold forming, is heated to a temperature above  $T_{trans}$ .

15 Shape-memory polymers in accordance with the present invention are polymers from which materials can be prepared which possess the property that they can be impressed with a desired shape (permanent shape), to which these materials, after deformation or after impressing a second shape (temporary shape), can 20 revert spontaneously and without external forces by means of simple warming or by means of another energetic stimulus. Deformation and retransformation (recovery) can be carried out over multiple cycles. The degree of attainability of the initial, permanent shape, is during a first relaxation cycle 25 consisting of deformation and recovery, usually somewhat smaller than during the subsequent cycles, most probably due to

the removal of existing textures, defects, etc., initially present. A very high degree of recovery will, however, be attained during the subsequent relaxation cycles. The degree of recovery during the first relaxation cycle is preferably at 5 least 30%, in particular at least 50% and the degree of recovery during the subsequent relaxation cycles is preferably at least 60%, more preferably at least 80%. This degree may, however, be also 90% or more. The degree of recovery can be measured in accordance with usual curl-retention measurements 10 by means of the determination of the length of a treated hair strand or by means of known, suitable stress-strain experiments.

The shape memory effect on hair is the property the a specific 15 hairdo (permanent memory shape) may be substantially recalled, after a deformation, spontaneously and without the application of any external forces by simple heating or some other energetic stimulus, i.e. to a degree during the first recovery cycle of at least 30%, preferably at least 50%, and to a 20 degree, during subsequent cycles of recovery of at least 60%, preferably at least 80% or 90%.

Macromers or pre-polymers in accordance with the present invention which can be crosslinked in order to provide shape-25 memory polymers, are polymers or oligomers wherein the fixation of an impressed, permanent shape occurs by means of chemical

bonds connecting specific polymer strands or oligomer strands.

The crosslinkage, by means of chemical bonds, can be provided by means of ionic or covalent bonds. The crosslinking reaction may be any suitable chemical reaction, for example, a salt

5 formation reaction, a condensation reaction, an addition reaction, a substitution reaction or a reaction initiated photochemically or by means of a radical. The crosslinking reaction can occur using suitable catalysts or initiators or the crosslinking reaction can occur without the use of a  
10 catalyst. The crosslinking reaction can be initiated by means of a suitable energy source, for example, electromagnetic radiation, ultrasound, heat or mechanical energy. A combination of two or more methods for initiation can be employed in order to increase the efficiency or the velocity of  
15 the crosslinking reaction.

Shape-memory polymers which can be used in accordance with the

present invention possess at least one transition temperature

$T_{trans}$ . This transition temperature may be a melting temperature

20  $T_m$  or a glass transition temperature  $T_g$ . Above  $T_{trans}$ , the polymer has a lower modulus of elasticity than below  $T_{trans}$ . The ratio of the modulus of elasticity below  $T_{trans}$  to above  $T_{trans}$  is preferably at least 20. The transition temperature  $T_{trans}$  is preferably above room temperature ( $20^\circ\text{C}$ ), preferably this  
25 transition temperature is at least  $30^\circ\text{C}$ , in particular preferred  $40^\circ\text{C}$ . The transition temperature  $T_{trans}$  is the

temperature above which the spontaneous recovery of the permanent shape, starting from the deformed shape or the temporary shape, occurs.

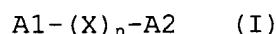
- 5 The terms "hairdos" or "shape of hair" in accordance with the present invention are to be understood broadly and comprise in particular also the degree of waviness or the degree of evenness of hair. A programmed hairdo in accordance with the present invention is any group of hairs which show a specific
- 10 shape due to shape-memory polymers which have been crosslinked and which fix a permanent shape. Recovery of a programmed hairdo in accordance with present invention means that the programmed hairdo is recovered after a deformation, to a degree of at least 60%, preferably to a degree of at least 80%, in
- 15 relation to the shape which can be obtained after a first relaxation cycle. The degree of recovery can, for example, be determined by means of the determination of the length of a hair strand or hair curl.
- 20 Suitable macromers or pre-polymers, which can be chemically crosslinked in order to provide shape-memory polymers are macromonomers which can be polymerized or which can be crosslinked by means of single chemical bonds. The chemically crosslinkable polymers are designated as thermoset polymers in
- 25 WO 99/42147. The macromers and thermoset polymers disclosed in WO 99/42147 are suitable for use in accordance with the present

invention and these materials are incorporated here by reference. Soft, thermoplastic segments (switching segments) having a transition temperature  $T_{trans}$  are crosslinked by means of chemical, preferably covalent bonds. Required are switching 5 segments and fixation points (network points). The fixation points fix the permanent form while the switching segments fix the temporary shape. The shape memory effect is based on the change of the elasticity at, above, or below  $T_{trans}$  or during the transition from above to below  $T_{trans}$  or from below to above 10  $T_{trans}$ . The ratio of the modulus of elasticity below  $T_{trans}$  to above  $T_{trans}$  is preferably at least 20. The higher this ratio is, the more expressed the shape-memory effect can be obtained. Four types of thermoset polymers having shape-memory properties can be designated:

15 Network polymers, penetrating network polymers, semi-interpenetrating networks and mixed penetrating networks. Network polymers can be formed by means of the covalent connection of macromonomers, i.e., of oligomers or polymers having reactive terminal groups, preferably ethylenically 20 unsaturated terminal groups, terminal groups which can be reacted by means of radical reactions or terminal groups which can be reacted by means of photochemical reactions. The crosslinking reaction can, for example, be initiated by means of light-sensitive or temperature-sensitive initiators, by 25 means of red-ox systems or combinations thereof, or the reaction can be initiated without the use of initiators, e.g.,

using UV light, heat or mechanical energy. Interpenetrating networks are formed at least two components which are each crosslinked but not with the other component. Mixed interpenetrating networks are formed using at least two 5 components, wherein one component is crosslinked by means of chemical bonds and the second component is crosslinked by means of physical interactions. Semi-interpenetrating networks are formed using at least two components, of which one is chemically crosslinkable, while the other one is not chemically 10 crosslinkable. Both components, however, cannot be separated from one another by means of physical methods.

In principle, all synthetic or natural oligomers or polymers having reactive terminal groups or side chain groups, which 15 provide the crosslinked shape-memory polymer with a suitable transition temperature  $T_{trans}$  and suitable moduli of elasticity above and below  $T_{trans}$  are suitable, wherein the terminal groups or the side chain groups are already present initially or are provided by means of a subsequent derivatization. These 20 materials allow a crosslinking reaction using the above-identified methods. Suitable macromers are, for example, macromers having the following formula



wherein A1 and A2 designate reactive, chemically crosslinkable groups and wherein

-(X)n- designates a divalent, thermoplastic polymer or oligomer segment. A1 and A2 are preferably acrylate or methacrylate

5 groups. The segment -(X)n- preferably designates a polyester segment, an oligoester segment, a polyalkylene glycol segment, an oligoalkylene glycol segment, a polyalkylene carbonate

segment or a oligoalkylene carbonate segment, wherein the alkylene groups are preferably ethylene groups or propylene

10 groups. Suitable macromonomers for the formation of thermoset polymers having shape-memory properties are oligo-(ε-

caprolactone) or poly(ε-caprolactone), oligolactide or

polylactide, oligoalkylene glycol, polyalkyleneglycol, e.g.,

polyethylene glycol or their block copolymers, wherein the

15 polymers or oligomers possess at least two ethylenically

unsaturated groups, which can be polymerized by means of a

radical reaction, e.g., acrylates or methacrylates, wherein

these groups are provided at a terminal position or at any side chain position.

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The polymer segments can be chosen among natural polymers, such as, for example, segments derived from proteins or polysaccharides. Suitable are also synthetic polymer segments.

Suitable natural polymer segments are proteins such as zein,

25 modified zein, casein, gelatine, gluten, serum albumin or collagen, as well as polysaccharides such as alginate,

cellulose, dextrane, pullulane or polyhyaluronic acid, as well as chitin, poly(3-hydroxyalkanoate), especially poly( $\beta$ -hydroxybutyrate), poly(3-hydroxyoctanoate) or poly(3-hydroxyfatty acids). Suitable are also derivatives of natural 5 polymer segments such as alkylated, hydroxyalkylated, hydroxylated or oxidated modifications.

Synthetically modified natural polymers are, for example, cellulose derivatives such as alkylcelluloses, 10 hydroxyalkylcelluloses, cellulose ethers, cellulose esters, nitrocellulose, chitosan or chitosan derivatives, which are, e.g., obtained by means of alkyl substitution or hydroxyalkyl substitution at the nitrogen and/or oxygen. Examples are methylcellulose, ethylcellulose, hydroxypropylcellulose, 15 hydroxypropylmethylcellulose, hydroxybutylmethylcellulose, celluloseacetate, cellulosepropionate, celluloseacetatebutyrate, celluloseacetatephthalate, carboxymethylcellulose, cellulosetriacetate or cellulosesulfate sodium salt. These materials are all designated in the 20 following as "celluloses."

Suitable synthetic polymer blocks include polyphosphazenes, poly(vinylalcohols), polyamides, polyesteramides, poly(amino-acids), polyanhydrides, polycarbonates, polyacrylates, poly-25 alkynes, polyacrylamides, polyalkylenglycoles, polyalkylen-oxides, polyalkylenterephthalates, polyorthoesters, polyvinyl-

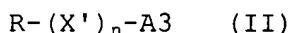
ethers, polyvinylesters, polyvinylhalogenides, polyvinylpyrrolidones, polyesters, polylactide, polyglycolide, polysiloxanes, polyurethanes and copolymers thereof. Examples of suitable polyacrylate are poly(methylmethacrylate), poly(ethylmethacrylate), poly(butylmethacrylate), poly(isobutylmethacrylate), poly(hexylmethacrylate), poly(isodecylmethacrylate), poly(laurylmethacrylate), poly(phenylmethacrylate), poly(methylacrylate), poly(isopropylacrylate), poly(isobutylacrylate) or poly(octadecylacrylate). Suitable synthetic, biologically degradable polymer segments are polyhydroxyacids such as polylactide, polyglycolide and and copolymers thereof, poly(ethylenterephthalate); poly(hydroxybuturic acid); poly(hydroxyvaleric acid); poly[lactide-co-( $\epsilon$ -caprolactone)]; poly[glycolide-co-( $\epsilon$ -caprolactone)]; polycarbonates, poly(aminoacids); poly(hydroxyalkanoates); polyanhydrides; poly-orthoesters as well as mixtures and copolymers thereof.

Examples of polymer segments which are less readily biologically degradable are poly(methacrylic acid), poly(acrylic acid), polyamides, polyethylene, polypropylene, polystyrene, polyvinylchloride, polyvinylphenol as well as mixtures and copolymers thereof.

In a preferred embodiment of the present invention, the composition comprises a mixture of (A) macromers which are substituted with at least two reactive, crosslinkable groups,

and (B) macromers, which are substituted with only one reactive group. Suitable additiona 1 macromers are, for example, macromers of the following general formula:

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wherein R designates a monovalent organic residue, A3 designates a reactive, chemically crosslinkable group and  $-(X')_n$  designates a divalent, thermoplastic polymer segment or 10 oligomer segment. A3 preferably represents an acrylate group or a methacrylate group. The segment  $-(X')_n$ - preferably represents a polyalkyleneglycol, monoalkylethers thereof, or block copolymers thereof, wherein the alkylene groups preferably are ethylene or propylene groups and wherein the 15 alkyl groups preferably comprise from 1 to 30 carbon atoms.

Particularly preferred are mixtures of (A) polyalkyleneglycoles or polycaprolactones having terminal ester groups comprising acrylic acid or methacrylic acid and (B) polyalkyleneglycol-20 monoalkylethers, having one terminal ester group comprising acrylic acid or methacrylic acid wherein the alkylene groups are preferably ethylene or propylene groups and the alkyl groups are preferably C1- bis C30-alkyl groups.

25 As component (A) the following are, e.g., suitable: poly( $\epsilon$ -caprolactone)-dimethacrylate, poly(DL-lactide)-dimethacrylate,

poly(L-lactide-co-glycolide)-dimethacrylate,  
poly(ethyleneglycol)dimethacrylate, poly(propylene-  
glycol)dimethacrylate, PEG-block-PPG-block-PEG-dimethacrylate,  
poly(ethyleneadipate)-dimethacrylate, hexamethylencarbonat-di-  
5 methacrylate.

Suitable as component (B) are, e.g., the following: poly-  
(ethyleneglycol)monoacrylate, poly(propyleneglycol)monoacrylate  
and monoalkylethers thereof.

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A further particular embodiment relates to a method of treating  
hair, comprising:

- applying a composition onto hair, comprising at least  
15 one shape memory polymer, which comprises at least two  
transition temperatures  $T_{trans}$  and  $T'_{trans}$ , and wherein  
this shape memory polymer comprises at least one hard  
segment with a first transition temperature  $T'_{trans}$ ,  
which is crosslinkable by means of physical  
20 interactions, wherein the first transition temperature  
is above room temperature, preferably more than 10 ° C  
above room temperature, and at least one soft segment  
having a second transition temperature  $T_{trans}$ , which lies  
below  $T'_{trans}$ , preferably at least 10° C below  $T'_{trans}$ ,

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- previously, at the same time or subsequently shaping the hair to a defined (permanent) shape and, subsequently, fixing the shape by means of a physical cross-linking of the shape memory polymer.

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The shaping of hair occurs suitably under warming to a temperature of at least  $T'$  <sub>trans</sub> and the shape of the hair is fixed by means of cooling to a temperature below  $T'$  <sub>trans</sub>. Room temperature in this connection refers generally to ambient 10 temperature, preferably at least 20 ° C and, in warmer climates, preferably at least 25 ° C. The application of the composition onto the hair can be carried out in different ways, for example directly by spraying or in an indirect manner by applying the composition first to the hand or a suitable device, for example 15 a comb, a brush etc, followed by a subsequent application within or onto the hair. The consistency of the composition may be the consistency of a solution, a dispersion, a lotion, a thickened lotion, a gel, a foam, a semi-solid composition, waxy or creamy.

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A further embodiment of the invention is a method for impressing a second hairdo over a programmed, recallable first hairdo. During this method the hairdo (permanent shape), programmed by means of the above-mentioned method, is warmed to 25 a temperature between  $T'$  <sub>trans</sub> and  $T$  <sub>trans</sub>. Subsequently the hair is

brought into the second (temporary) shape and this second shape is fixed by means of cooling to a temperature below  $T_{trans}$ .

A further embodiment of the present invention is a method for  
5 recalling a programmed first hairdo (permanent shape), prepared  
by means of the above -mentioned method. In this method the  
hairdo in a temporary shape or in the shape of a hairdo being  
obtained by cold -forming, is warmed to a temperature above  
 $T_{trans}$ . The permanent shape is formed spontaneously and without  
10 further external influence. Cold -forming of a hairdo is a  
change of the hairdo at ambient temperature, without the use of  
additional heating by means of a hairdryer or similar devices.  
The deformation can, for example, be carried out mechanically,  
for example be means of subjecting the curls to gravity , by  
15 means of combing or brushing the hair, due to the influence of  
wind or humidity, due to mechanical influences during sleep or  
during lying.

The invention furthermore relates to a method for reprogramming  
20 a permanent hairdo, obtained with the above -mentioned method,  
into a different, new permanent shape. In order to achieve  
this goal, the initial hairdo is warmed to a temperature above  
 $T'_{trans}$  and the hair is brought into a new shape. Subsequently  
this new form is fixed by means of cooling to a tempe rature  
25 below  $T'_{trans}$ .

Shape memory polymers which may be crosslinked physically in accordance with the present invention are polymers, with which the fixation of the impressed permanent shape due to crosslinking occurs by physical interactions. A crosslinking 5 by means of physical interactions can be achieved for example when specific segments of the polymer chains are assembled together in crystalline areas. The physical interactions may be charge transfer complexes, hydrogen bonds, dipolar or hydrophobic interactions, Van der Waals interactions or ionic 10 interactions of polyelectrolyte segments. These interactions may occur between different segments within one polymer strand (intramolecular) and/or between different polymer strands (intermolecular). The formation of the interactions may be initiated by means of cooling (in particular in relation to 15 crystallisation) and/or by means of drying, i.e. the removal of solvents.

Shape memory polymers which may be crosslinked physically and which are suitable in accordance with the present invention do 20 show at least two transition temperatures  $T_{trans}$  and  $T'_{trans}$ . The two transition temperatures may for example be melting temperatures  $T_m$  or glass transition temperatures  $T_g$ . Above  $T_{trans}$  the polymer does show a lower modulus of elasticity compared 25 with the modulus of elasticity below  $T_{trans}$ . The ratio of the moduli of elasticity below and above  $T_{trans}$  preferably is at least 10, more preferably at least 20. The lower transition

temperature  $T_{trans}$  preferably is higher than room temperature ( $20^\circ C$ ), in particular at least  $30^\circ C$ , more preferably at least  $35^\circ C$  or at least  $40^\circ C$  and this temperature is the temperature at which the spontaneous recovery of the permanent shape from 5 the deformed or temporary shape occurs.  $T_{trans}$  is preferably above the usually to be expected ambient temperatures, so that at ambient temperatures no significant, undesired, thermally induced deformation of the temporary hairdo occurs. Suitable ranges for  $T_{trans}$  are for example from 25 to  $100^\circ C$ , from 30 to 10  $75^\circ C$ , from 35 to  $70^\circ C$  or from 40 to  $60^\circ C$ .

The upper transition temperature  $T'_{trans}$  is higher than  $T_{trans}$  and this transition temperature is the temperature above which the impression of the permanent shape or the reprogramming of a 15 permanent shape into a new permanent shape occurs and below which the permanent shape is fixed.  $T'_{trans}$  preferably is to the extend higher than  $T_{trans}$ , so that during the warming of the hairdo to a temperature above  $T_{trans}$ , for the recovery of the permanent shape or for the reforming of a temporary hairdo 20 while maintaining the permanent shape, no significant, undesired, thermally induced deformation of the permanent shape occurs. Preferably,  $T'_{trans}$  is at least  $10^\circ C$ , more preferably at least  $20^\circ C$  or at least  $30^\circ C$  above  $T_{trans}$ . The difference between  $T'_{trans}$  and  $T_{trans}$  may be for example from 10 to  $80^\circ C$ , 25 from 20 to  $70^\circ C$  or from 30 to  $60^\circ C$ . Suitable ranges for  $T'_{trans}$

are for example from 40 to 150 ° C from 50 to 100 ° C or from 70 to 95° C.

Suitable shape memory polymers which may be crosslinked physically are polymers which consist of at least one hard segment and at least one soft segment. The hard segment shows physical crosslinks and has a transition temperature  $T'$  <sup>trans</sup> which is above room temperature, preferably more than 10 ° C above 20 ° C. The soft segment has a transition temperature  $T_{trans}$  which is below  $T'$  <sup>trans</sup>, preferably at least 10 ° C below  $T'$  <sup>trans</sup>. The polymer segments are preferably oligomers, in particular linear chain molecules having a molecular weight of for example 400 to 30,000 preferably 1,000 to 20,000 or 1,500 to 15,000. These polymers may be linear di -block tri -block, tetra-block or multi -block copolymers, they may be branched, dendritic or graft copolymers. Preferably these polymers are not linear polyurethanes comprising bis(2 -hydroxy-ethyl)-hydroquinone. The molecular weight of the polymers may for example be from 30,000 to 1,000,000, preferably from 50,000 to 700,000 or from 70,000 to 400,000. Suitable shape memory polymers which may be crosslinked physically are disclosed in WO 99/42147 and these polymers are disclosed there as thermoplastic polymers. The thermoplastic polymers disclosed in WO 99/42147 as well as the methods of preparation are suitable in accordance with the present invention and this disclosure is herewith incorporated by reference. These

polymers do show a degree of crystallinity of preferably 3 to 80%, more preferably 3 to 60%. The ratio of the moduli of elasticity below and above  $T_{trans}$  preferably is at least 10, more preferably at least 20. The polymer segments may be segments 5 derived from natural polymers, such as proteins or polysaccharides. The segments may also be synthetic polymer blocks. Suitable natural or synthetic polymer segments are identical with the crosslinkable macromers named above.

10 Suitable shape memory polymers are in particular multiblock copolymers, comprising at least one first type of blocks and at least one different second type of blocks, wherein the blocks do enable that the multiblock copolymer possesses two different transition temperatures. Suitable multiblock copolymers are in 15 particular copolymers prepared from at least two different macrodiols and at least one diisocyanate. Macrodiols are oligomers or polymers having at least two free hydroxyl groups. Oligomers do consist usually of at least two, preferably at least 3, more preferably 4 to 20, 5 to 15 or 6 to 20 10 monomers. The macrodiols may possess the general formula HO-A-OH, wherein A defines a divalent, oligomeric or polymeric group, preferably a polyester or an oligoester. The diisocyanate may have the general formula OCN -B-NCO, wherein B defines a divalent organic group, preferably an alkylene group 25 or an arylene group, which may be further substituted. The alkylene group may be linear, branched or cyclic and this group

preferably possesses 1 to 30 carbon atoms, more preferably 2 to 20 or 5 to 15 carbon atoms.

Particularly preferred shape memory polymers are the

5 copolyester urethanes disclosed in WO 99/42147, in particular the reaction products of (a) two different macrodiols, selected among  $\alpha$ ,  $\omega$ -dihydroxy polyesters,  $\alpha$ ,  $\omega$ -dihydroxy oligoesters,  $\alpha$ ,  $\omega$ -dihydroxy polylactones and  $\alpha$ ,  $\omega$ -dihydroxy oligolactones, and (b) at least one diisocyanate, preferably

10 trimethylhexane-1,6-diisocyanate. In particular preferred are macrodiols from poly(para-dioxanone) (PDX), poly(pentadecalactone) (PDL), poly( $\epsilon$ -caprolactone) (PCL), poly(L-lactide-co-glydolide) (PLGA). The molecular weights of the macrodiols are preferably within the range of from 400 to

15 30,000, preferable 1,000 to 20,000 or 1,500 to 15,000. The molecular weights of the resulting multiblock copolymers are

preferably  $M_w$  from 30,000 to 1,000,000, more preferably from 50,000 to 70,000 or from 70,000 to 400,000 g/mol, as determined by GPC. The polydispersity preferably is within the range of

20 from 1.7 to 2.0.

One further preferred embodiment is concerned with a method for hair treatment using a composition comprising at least two compounds, which alone do show only minute or no shape memory

25 properties but which, when applied in combination according to

the method of the present invention provide the hair with a synergistically enhanced shape memory effect.

Compositions in accordance with present invention for the

5 treatment of hair comprise at least one of the above-mentioned macromers or pre-polymers, which is suitable to be crosslinked in order to provide shape-memory polymers, in an amount of preferably from 0.01 to 25 weight %, more preferably of from 0.1 to 15 weight % in a suitable liquid medium. The

10 composition can be provided in the form of a solution, dispersion, emulsion, suspension or latex. The liquid medium is preferably cosmetically acceptable and physiologically acceptable.

15 The composition in accordance with present invention usually is present in the form of a solution or dispersion comprising a suitable solvent. Preferred are in particular aqueous, alcoholic or aqueous-alcoholic solvents. Suitable solvents are, e.g., aliphatic alcohols having from 1 to 4 carbon atoms

20 or a mixture of water with at least one of these alcohols. Other organic solvents can, however, also be employed, in particular linear or branched hydrocarbons, such as pentane, hexane, isopentane, cyclic hydrocarbons such as cyclopentane and cyclohexane, organic linear or cyclic ethers, such as

25 tetrahydrofuran (THF) or liquid organic esters, such as ethylacetate. Furthermore, solvents on the basis of silicone

materials are suitable, in particular silicone oils on the basis of linear or cyclic polydimethylsiloxanes (dimethicone or Cyclomethicone). The solvents are preferably present in an amount from 0,5 to 99 weight %, more preferably in an amount

5 from 40 to 90 weight %.

The compositions in accordance with present invention may comprise in addition from 0.01 to 25 weight % of at least one hair fixative, hair coloring agent and/or hair cosmetic. Hair

10 fixatives are in particular the known conventional film-forming hair fixative polymers. The film forming and hair fixative polymer may be of synthetic origin or of natural origin and may be of nonionic, cationic, anionic or amphoteric character.

Such a polymer additive, which can be present in an amount of

15 from 0.01 to 25 weight %, preferably 0.1 to 20 weight %, more preferably 0.5 to 15 weight %, may also comprise a mixture of more than one polymers, and this additive can be modified further with respect to the hair fixative properties by means of the addition of further polymers having a thickening effect.

20 Film-forming, hair fixative polymers in accordance with present invention are polymers which are able, when employed in aqueous, alcoholic or aqueous-alcoholic solutions at a concentration of from 0.01 to 5%, to provide a polymer film on the hair in order to provide fixative properties.

As suitable, synthetic, nonionic, film-forming, hair fixative polymers, the hair treatment composition in accordance with present invention may comprise homo polymers of vinyl pyrrolidone, homopolymers of N-vinylformamide, copolymers of 5 vinylpyrrolidone and vinylacetate, terpolymers of vinylpyrrolidone, vinylacetate and vinylpropionate, polyacrylamide, polyvinylalcohols, or polyethyleneglycols having a molecular weight of from 800 to 20.000 g/mol.

Suitable, synthetic, anionic, film-forming polymers are 10 crotonic acid/vinylacetate copolymers and terpolymers of acrylic acid, ethylacrylate and N-t-butylacrylamide. Natural film-forming polymers or polymers obtained therefrom by means of chemical derivatization may also be employed in the hair treatment composition in accordance with present invention. In 15 this respect low molecular chitosane having a molecular weight of from 30,000 to 70,000 g/mol or high molecular chitosane, derivatives of chitosane soluble in organic solvents, mixtures of oligosaccharides, monosaccharides, and disaccharides, China balsam resin, cellulose derivatives such as 20 hydroxypropylcellulose having a molecular weight of from 30,000 to 50,000 g/mol, or shellac in its neutralized or unneutralized form are known as suitable. Amphoteric polymers can also be employed in the hair treatment composition in accordance with present invention. Suitable are, e.g., copolymers of 25 octylacrylamide, t-butylaminoethylmethacrylate and two or more

monomers selected from the group consisting of acrylic acid, methacrylic acid and simple esters thereof.

Cationic polymers which can be used in accordance with present invention comprise copolymers of vinylpyrrolidones with 5 quaternized derivatives of dialkylaminoacrylate and dialkylaminomethacrylate, such as, for example, the copolymer of vinylpyrrolidone and dimethylaminomethacrylate quaternized with diethylsulfate. Further cationic polymers are copolymers 10 of vinylpyrrolidone with vinylimidazoliummethochloride, the terpolymer of dimethyldiallylammoniumchloride, sodiumacrylate and acrylamide, the terpolymer of vinylpyrrolidone, dimethylaminoethylmethacrylate and vinylcarprolactam, the quaternized ammonium salt, prepared from hydroxyethylcellulose and a 15 trimethylammonium substituted epoxide, the vinylpyrrolidone and methacrylamidopropyltrimethylammoniumchloride and diquaternized polydimethylsiloxanes.

The consistency of hair treatment compositions in accordance 20 with present invention can be improved by means of the addition of thickeners. In this respect, homopolymers of acrylic acid having a molecular weight of 2,000,000 to 6,000,000 g/mol are suitable. Further copolymers of acrylic acid and acrylamide (sodium salt) having a molecular weight of from 2,000,000 to 25 6,000,000 g/mol, sclerotium gum and copolymers of acrylic acid and methacrylic acid are suitable.

A cosmetic composition in accordance with present invention can be employed in the form of different formulations for different types of applications, e.g., as lotion, as spray lotion, as 5 cream, as gel, as foam-gel, as aerosol spray, as non-aerosol spray, as aerosol foam, as non-aerosol foam, as o/w- or w/o-emulsion, as micro emulsion or as hair wax.

When the hair treatment composition in accordance with present 10 invention is provided in the form of an aerosol spray, the composition comprises additionally from 15 to 85 weight %, preferably from 25 to 75 weight % of a propellant and the composition is filled into a pressurized canister having a spray button. As propellants, lower alkanes, such as n-butane, 15 isobutene and propane as well as mixtures thereof as well as dimethylether or fluorohydrocarbons, such as F 152a (1,1-difluorethane) or F 134 (tetrafluorethane) are suitable, as well as propellants which are present at the pressures in question in gaseous forms such as N<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub> as well as 20 mixtures of the above-mentioned propellants.

When the hair treatment composition of the present invention is provided in the form of a sprayable non-aerosol hair spray, the composition is sprayed by means of a suitable, mechanical 25 spraying device. Spray devices of the mechanical type are devices which allow the spraying of a composition without using

a propellant. Suitable mechanical spray devices are, e.g., spray pumps or elastic containers provided with a spray valve, into which the cosmetic composition in accordance with present invention is filled under pressure, whereby the elastic 5 container is expanded and wherein the cosmetic composition is continuously discharged if the valve is open, due to the contraction of the elastic container.

When the hair treatment composition in accordance with present 10 invention is provided in the form of a hair foam (mousse), the composition comprises at least one conventional foaming agent known in the art for this purpose. The composition is foamed with or without the aid of propellants or chemical propellants and the foam may be applied to the hair and may remain in the 15 hair without the need of rinsing the hair. A product in accordance with present invention comprises as additional component a device for the provision of a foam of the composition. Devices for providing a foam are devices which allow the provision of a foam starting from a liquid, with or 20 without the use of a propellant. Suitable mechanical foaming devices are, e.g., usual foam pumps, or usual aerosol foaming heads.

When the hair treatment composition in accordance with present 25 invention is provided in the form of a hair gel, it comprises at least one gel forming substance in an amount of preferably

from 0.05 to 10, more preferably from 0.1 to 2 weight %. The viscosity of the gel preferably amounts to from 100 bis 50,000 mm<sup>2</sup>/s, more preferably 1,000 bis 15,000 mm<sup>2</sup>/s at 25°C, measured as dynamic viscosity using a Bohlin Rheometer CS, 5 measurement body C25 using a shear velocity of 50 s<sup>-1</sup>.

When the hair treatment composition in accordance with present invention is provided in the form of a hair wax, it comprises additionally water-unsoluble fatty substances or waxy 10 substances, or substances which provide the composition with a waxy consistence, in an amount of preferably 0.5 bis 30 weight %. Suitable water unsoluble substances are, for example, emulgators having a HLB-value of below 7, silicone oils, silicone waxes, wax materials (e.g., waxy alcohols, waxy acids, 15 waxy esters, as well as natural waxes such as beeswax, Carnauba wax, etc.), fatty alcohols, fatty acids, fatty acid esters or high molecular polyethyleneglycols having a molecular weight of from 800 bis 20,000, preferably from 2,000 to 10,000 g/mol.

20 When the hair treatment composition in accordance with present invention is provided in the form of a hair lotion, it is present as a substantially non-viscous or low viscosity, flowable solution, dispersion or emulsion comprising a content of at least 10 weight %, preferably 20 to 95 weight % of a 25 cosmetically acceptable alcohol. As alcohols, the usual

alcohols used for cosmetic purposes can be named, in particular the lower C1 to C4 alcohols such as ethanol and isopropanol.

When the hair treatment composition of the present invention is 5 present in the form of a hair cream, it is preferably provided in the form of an emulsion and it either comprises additional viscosity providing components in an amount of from 0.1 to 10 weight % or the required viscosity and creamy consistency is obtained by means of micelle formation using suitable 10 emulsifiers, fatty acids, fatty alcohols, waxes, etc.

In a preferred embodiment the composition in accordance with present invention is provided in a form enabling, at the same time, the impression of a recallable hairdo as well as 15 providing hair coloration. The composition is then formulated as coloring hair treatment composition, e.g., as coloring fixative, coloring cream, coloring foam, etc. It comprises at least one coloring component. The coloring component may be an organic dye, in particular direct dyes or it may be an 20 inorganic pigment.

The total amount of coloring agent amounts in the composition in accordance with present invention to about 0.01 to 7 weight %, preferably about 0.2 to 4 weight %. Suitable direct 25 colorants to be used in the composition in accordance with present invention are, e.g., triphenylmethane colorants,

aromatic nitro colorants, azo colorants, quinone colorants, cationic or anionic colorants. Suitable are the following:

Nitro dyes (blue):

5 1,4-bis[(2-hydroxyethyl)amino]-2-nitrobenzene, 1-(2-hydroxyethyl)amino-2-nitro-4-[di(2-hydroxyethyl)amino]-benzene (HC Blue No. 2), 1-amino-3-methyl-4-[(2-hydroxyethyl)amino]-6-nitrobenzene (HC Violet No. 1), 4-[ethyl-(2-hydroxyethyl)-amino]-1-[(2-hydroxyethyl)amino]-2-nitrobenzene-hydrochloride

10 10 (HC Blue No. 12), 4-[di(2-hydroxyethyl)amino]-1-[(2-methoxyethyl)amino]-2-nitrobenzene (HC Blue No. 11), 1-[(2,3-di-hydroxypropyl)amino]-4-[methyl-(2-hydroxyethyl)amino]-2-nitrobenzene (HC Blue No. 10), 1-[(2,3-dihydroxypropyl)amino]-4-[ethyl-(2-hydroxyethyl)amino]-2-nitrobenzene-hydrochloride

15 15 (HC Blue No. 9), 1-(3-hydroxypropylamino)-4-[di(2-hydroxyethyl)amino]-2-nitrobenzene (HC Violet No. 2), 1-methylamino-4-[methyl-(2,3-dihydroxypropyl)amino]-2-nitrobenzene (HC Blue No. 6), 2-((4-amino-2-nitrophenyl)amino)-5-dimethylamino-benzoic acid (HC Blue No. 13), 1-(2-aminoethyl-amino)-4-[di(2-hydroxyethyl)amino]-2-nitrobenzene, 4-(di(2-hydroxyethyl)amino)-2-nitro-1-phenylamino-benzene.

Nitro dyes (red):

1-amino-4-[(2-hydroxyethyl)amino]-2-nitrobenzene (HC Red No. 25 7), 2-amino-4,6-dinitro-phenene, 1,4-diamino-2-nitrobenzene (CI76070), 4-amino-2-nitro-diphenylamine (HC Red No. 1), 1-

amino-4-[di(2-hydroxyethyl)amino]-2-nitrobenzene-hydrochloride (HC Red No. 13), 1-amino-5-chlor-4-[(2-hydroxyethyl)amino]-2-nitrobenzene, 4-amino-1-[(2-hydroxyethyl)amino]-2-nitrobenzene (HC Red No. 3), 4-((2-hydroxyethyl)methylamino)-1-  
5 (methylamino)-2-nitrobenzene, 1-amino-4-((2,3-dihydroxy-  
propyl)amino)-5-methyl-2-nitrobenzene, 1-amino-4-(methylamino)-  
2-nitrobenzene, 4-amino-2-nitro-1-((prop-2-en-1-yl)amino)-  
benzene, 4-amino-3-nitrophenene, 4-[(2-hydroxyethyl)amino]-3-  
nitrophenene, 4-[(2-nitrophenyl)amino]phenene (HC Orange No.  
10 1), 1-[(2-aminoethyl)amino]-4-(2-hydroxyethoxy)-2-nitrobenzene  
(HC Orange No. 2), 4-(2,3-dihydroxypropoxy)-1-[(2-  
hydroxyethyl)amino]-2-nitrobenzene (HC Orange No. 3), 1-amino-  
5-chlor-4-[(2,3-dihydroxypropyl)amino]-2-nitrobenzene (HC Red  
No. 10), 5-chlor-1,4-[di(2,3-dihydroxypropyl)amino]-2-  
15 nitrobenzene (HC Red No. 11), 2-[(2-hydroxyethyl)amino]-4,6-  
dinitro-phenene, 4-ethylamino-3-nitrobenzoic acid, 2-[(4-amino-  
2-nitrophenyl)amino]-benzoic acid, 2-chlor-6-ethylamino-4-  
nitrophenene, 2-amino-6-chlor-4-nitrophenene, 4-[(3-  
hydroxypropyl)amino]-3-nitrophenene, 2,5-diamino-6-nitro-  
20 pyridine, 6-amino-3-[(2-hydroxyethyl)amino]-2-nitropyridine, 3-  
amino-6-[(2-hydroxyethyl)amino]-2-nitropyridine, 3-amino-6-  
(ethylamino)-2-nitropyridine, 3-[(2-hydroxyethyl)amino]-6-  
(methylamino)-2-nitropyridine, 3-amino-6-(methylamino)-2-  
nitropyridine, 6-(ethylamino)-3-[(2-hydroxyethyl)amino]-2-  
25 nitropyridine, 1,2,3,4-tetrahydro-6-nitrochinoxaline, 7-amino-  
3,4-dihydro-6-nitro-2H-1,4-benzoxazin (HC Red No. 14).

## Nitro dyes (yellow):

1,2-diamino-4-nitrobenzene (CI76020), 1-amino-2-[(2-hydroxyethyl)amino]-5-nitrobenzene (HC Yellow No. 5), 1-(2-hydroxyethoxy)-2-[(2-hydroxyethyl)amino]-5-nitrobenzene (HC Yellow No. 4), 1-[(2-hydroxyethyl)amino]-2-nitrobenzene (HC Yellow No. 2), 2-(di(2-hydroxyethyl)amino)-5-nitrophenene, 2-[(2-hydroxyethyl)amino]-1-methoxy-5-nitrobenzene, 2-amino-3-nitrophenene, 1-amino-2-methyl-6-nitrobenzene, 1-(2-hydroxyethoxy)-3-methylamino-4-nitrobenzene, 2,3-(dihydroxypropoxy)-3-methylamino-4-nitrobenzene, 2-[(2-hydroxyethyl)amino]-5-nitrophenene (HC Yellow No. 11), 3-[(2-aminoethyl)amino]-1-methoxy-4-nitrobenzene-hydrochloride (HC Yellow No. 9), 1-[(2-Ureidoethyl)amino]-4-nitrobenzene, 4-[(2,3-dihydroxypropyl)-amino]-3-nitro-1-trifluormethyl-benzene (HC Yellow No. 6), 1-chlor-2,4-bis[(2-hydroxyethyl)amino]-5-nitrobenzene (HC Yellow No. 10), 1-amino-4-((2-aminoethyl)amino)-5-methyl-2-nitrobenzene, 4-[(2-hydroxyethyl)amino]-3-nitro-1-methylbenzene, 1-chlor-4-[(2-hydroxyethyl)amino]-3-nitrobenzene (HC Yellow No. 12), 4-[(2-hydroxyethyl)amino]-3-nitro-1-trifluormethyl-benzene (HC Yellow No. 13), 4-[(2-hydroxyethyl)-amino]-3-nitro-benzonitril (HC Yellow No. 14), 4-[(2-hydroxyethyl)amino]-3-nitro-benzamide (HC Yellow No. 15) 3-((2-hydroxyethyl)amino)-4-methyl-1-nitrobenzene, 4-chlor-3-((2-hydroxyethyl)amino)-1-nitrobenzene.

## Quinone dyes:

1, 4-di[(2, 3-dihydroxypropyl)amino]-9, 10-anthraquinone, 1, 4-di[(2-hydroxyethyl)amino]-9, 10-anthraquinone (CI61545, Disperse Blue 23), 1-[(2-hydroxyethyl)amino]-4-methylamino-9, 10-anthraquinone (CI61505, Disperse Blue No. 3), 2-[(2-aminoethyl)amino]-9, 10-anthraquinone (HC Orange No. 5), 1-amino-4-hydroxy-9, 10-anthraquinone (CI60710, Disperse Red 15), 1-hydroxy-4-[(4-methyl-2-sulfophenyl)amino]-9, 10-anthraquinone, 7-beta-D-glucopyranosyl-9, 10-dihydro-1-methyl-9, 10-dioxo-3, 5, 6, 8-tetrahydroxy-2-antracencarboxylic acid (CI75470, Natural Red 4), 1-[(3-aminopropyl)amino]-4-methylamino-9, 10-anthraquinone (HC Blue No. 8), 1-[(3-aminopropyl)amino]-9, 10-anthraquinone (HC Red No. 8), 1, 4-diamino-2-methoxy-9, 10-anthraquinone (CI62015, Disperse Red No. 11, Solvent Violet No. 26), 1, 4-dihydroxy-5, 8-bis[(2-hydroxyethyl)amino]-9, 10-anthraquinone (CI62500, Disperse Blue No. 7, Solvent Blue No. 69), 1, 4-diamino-9, 10-anthraquinone (CI61100, Disperse Violet No. 1), 1-amino-4-(methylamino)-9, 10-anthraquinone (CI61105, Disperse Violet No. 4, Solvent Violet No. 12), 2-hydroxy-3-methoxy-1, 4-naphthoquinone, 2, 5-dihydroxy-1, 4-naphthoquinone, 2-hydroxy-3-methyl-1, 4-naphthoquinone, N-(6-((3-chlor-4-(methylamino)phenyl)imino)-4-methyl-3-oxo-1, 4-cyclohexadien-1-yl)urea (HC Red No. 9), 2-((4-(di(2-hydroxyethyl)amino)-phenyl)amino)-5-((2-hydroxyethyl)amino)-2, 5-cyclohexadien-1, 4-dion (HC Green No. 1), 5-hydroxy-1, 4-naphthoquinone (CI75500, Natural Brown No. 7), 2-hydroxy-1, 4-naphthoquinone (CI75480,

Natural Orange No. 6), 1,2-dihydro-2-(1,3-dihydro-3-oxo-2H-indol-2-yliden)-3H-indol-3-on (CI73000), 4-((5-((2-hydroxyethyl)amino-1-methyl-1H-pyrazol-4-yl)imino)-4,5-dihydro-5-((2-hydroxyethyl)imino)-1-methyl-1H-pyrazol-5

5 sulfate(1:1), hydrate(1:1).

Basic dyes:

9-(dimethylamino)-benzo[a]phenoxazin-7-ium-chloride (CI51175; Basic Blue No. 6), di[4-(diethylamino)phenyl][4-(ethylamino)naphthyl]carbenium-chloride (CI42595; Basic Blue No. 7), di-(4-(dimethylamino)phenyl)-(4-(methyl-phenylamino)naphthalin-1-yl)carbenium-chloride (CI42563; Basic Blue No. 8), 3,7-di(dimethylamino)phenothiazin-5-ium-chloride (CI52015 Basic Blue No. 9), di[4-(dimethylamino)phenyl][4-(phenylamino)naphthyl]carbenium-chloride (CI44045; Basic Blue No. 26), 2-[(4-(ethyl(2-hydroxyethyl)amino)phenyl)azo]-6-methoxy-3-methyl-benzothiazolium-methysulfate (CI11154; Basic Blue No. 41), 8-amino-2-brom-5-hydroxy-4-imino-6-[(3-(trimethylammonio)phenyl)amino]-1(4H)-naphthalinon-chloride (CI56059; Basic Blue No. 99), bis[4-(dimethylamino)phenyl][4-(methylamino)phenyl]carbenium-chloride (CI42535; Basic Violet No. 1), Tri(4-amino-3-methylphenyl)carbenium-chloride (CI42520; Basic Violet No. 2), Tris[4-(dimethylamino)phenyl]carbenium-chloride (CI42555; Basic Violet No. 3), 2-[3,6-(diethylamino)dibenzopyranium-9-yl]-benzoic acidchloride (CI45170; Basic Violet No. 10), di(4-aminophenyl)(4-amino-3-

methylphenyl)carbeniumchloride (CI42510 Basic Violet No. 14),  
1,3-bis[(2,4-diamino-5-methylphenyl)azo]-3-methylbenzol  
(CI21010; Basic Brown No. 4), 1-[(4-aminophenyl)azo]-7-(tri-  
methylammonio)-2-naphthol-chloride (CI12250; Basic Brown No.  
5 16), 3-[(4-amino-2,5-dimethoxyphenyl)azo]-N,N,N-trimethyl-  
benzeneaminiumchloride (CI112605, Basic Orange No. 69), 1-[(4-  
amino-2-nitrophenyl)azo]-7-(trimethylammonio)-2-naphthol-  
chloride, 1-[(4-amino-3-nitrophenyl)azo]-7-(trimethylammonio)-  
2-naphthol-chloride (CI12251; Basic Brown No. 17), 3,7-diamino-  
10 2,8-dimethyl-5-phenylphenazinium-chloride (CI50240; Basic Red  
No. 2), 1,4-dimethyl-5-[(4-(dimethylamino)phenyl)azo]-1,2,4-  
triazolium-chloride (CI11055; Basic Red No. 22), 2-hydroxy-1-  
[(2-methoxyphenyl)azo]-7-(trimethylammonio)-naphthalin-chloride  
(CI12245; Basic Red No. 76), 2-[2-((2,4-  
15 dimethoxyphenyl)amino)ethenyl]-1,3,3-trimethyl-3H-indol-1-ium-  
chloride (CI48055; Basic Yellow No. 11), 3-methyl-1-phenyl-4-  
[(3-(trimethylammonio)phenyl)azo]-pyrazol-5-one-chloride  
(CI12719; Basic Yellow No. 57), di[4-  
(dimethylamino)phenyl]iminomethan-hydrochloride (CI41000; Basic  
20 Yellow No. 2), bis[4-(diethylamino)phenyl]phenylcarbenium-  
hydrogensulfate (1:1) (CI42040; Basic Green No. 1), di(4-  
(dimethylamino)phenyl)-phenylmethanol (CI42000; Basic Green No.  
4), 1-(2-morpholiniumpropylamino)-4-hydroxy-9,10-anthraquinone-  
methylsulfate, 1-[(3-(dimethyl-propylaminium)propyl)amino]-4-  
25 (methylamino)-9,10-anthraquinone-chloride.

## Neutral azo dyes:

1-[di(2-hydroxyethyl)amino]-3-methyl-4-[(4-nitrophenyl)azo]-benzene (CI11210, Disperse Red No. 17), 1-[di(2-hydroxyethyl)amino]-4-[(4-nitrophenyl)azo]-benzene (Disperse Black No.

5 9), 4-[(4-aminophenyl)azo]-1-[di(2-hydroxyethyl)amino]-3-methylbenzene (HC Yellow No. 7), 2,6-diamino-3-[(pyridin-3-yl)azo]-pyridine, 2-((4-(acetylamino)phenyl)azo)-4-methyl-phenene (CI11855; Disperse Yellow No. 3).

## 10 Acidic dyes:

6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalene-sulfonic acid-disodium salt (CI15985; Food Yellow No. 3; FD&C Yellow No. 6),

2,4-dinitro-1-naphthol-7-sulfonic acid-disodium salt (CI10316; Acid Yellow No. 1; Food Yellow No. 1), 2-(Indan-1,3-dion-2-

15 yl)chinoline- $\alpha$ , $\alpha$ -sulfonic acid (mixture of mono- and disulfonic acid) (CI47005; D&C Yellow No. 10; Food Yellow No. 13; Acid Yellow No. 3), 5-hydroxy-1-(4-sulfophenyl)-4-[(4-sulfophenyl)azo]pyrazol-3-carboxylic acid-trisodium salt

(CI19140; Food Yellow No. 4; Acid Yellow No. 23), 9-(2-

20 Carboxyphenyl)-6-hydroxy-3H-xanthen-3-one (CI45350; Acid Yellow No. 73; D&C Yellow No. 8), 4-((4-amino-3-sulfo-phenyl)azo)benzenesulfonic acid-disodium salt (CI13015, Acid Yellow No. 9), 5-[(2,4-dinitrophenyl)amino]-2-phenylamino-

benzenesulfonic acid-sodium salt (CI10385; Acid Orange No. 3),

25 4-[(2,4-dihydroxyphenyl)azo]-benzenesulfonic acid monosodium salt (CI14270; Acid Orange No. 6), 4-[(2-hydroxynaphth-1-

yl)azo]-benzenesulfonic acid-sodium salt (CI15510; Acid Orange No. 7), 4-[(2,4-dihydroxy-3-[(2,4-dimethylphenyl)azo]-phenyl)azo]-benzenesulfonic acid-sodium salt (CI20170; Acid Orange No. 24), 4-hydroxy-3-[(4-sulfonaphth-1-yl)azo]-1-naphthaline-sulfonic acid-disodium salt (CI14720; Acid Red No. 14), 4-hydroxy-3-[(2-methoxyphenyl)azo]-1-naphthaline-sulfonic acid-monosodium salt (CI14710; Acid Red No. 4), 6-hydroxy-5-[(4-sulfonaphth-1-yl)azo]-2,4-naphthaline-disulfonic acid-trisodium salt (CI16255; Ponceau 4R; Acid Red No. 18), 3-hydroxy-4-[(4-sulfonaphth-1-yl)azo]-2,7-naphthaline-disulfonic acid-trisodium salt (CI16185; Acid Red No. 27), 8-amino-1-hydroxy-2-(phenylazo)-3,6-naphthaline-disulfonic acid-disodium salt (CI17200; Acid Red No. 33), 5-(acetylamino)-4-hydroxy-3-[(2-methylphenyl)azo]-2,7-naphthaline-disulfonic acid-disodium salt (CI18065; Acid Red No. 35), 2-(3-hydroxy-2,4,5,7-tetraiod-dibenzopyran-6-on-9-yl)-benzoic acid-disodium salt (CI45430; Acid Red No. 51), N-[6-(diethylamino)-9-(2,4-disulfophenyl)-3H-xanthen-3-yliden]-N-ethylethanammonium-hydroxide, internal salt, Sodium salt (CI45100; Acid Red No. 52), 8-[(4-Phenylazo)phenyl]azo]-7-naphthol-1,3-disulfonic acid-disodium salt (CI27290; Acid Red No. 73), 2',4',5',7'-tetrabrom-3',6'-dihydroxyspiro[isobenzofuran-1(3H),9'-[9H]xanthen]-3-on-disodium salt (CI45380 Acid Red No. 87), 2',4',5',7'-tetrabrom-4,5,6,7-tetrachlor-3',6'-dihydroxyspiro[isobenzofuran-1(3H),9'[9H]xanthen]-3-on-disodium salt (CI45410; Acid Red No. 92), 3',6'-dihydroxy-4',5'-diiodospiro[isobenzofuran-

1(3H),9'(9H)-xanthen]-3-on-disodium salt (CI45425; Acid Red No. 95), 2-hydroxy-3-((2-hydroxynaphth-1-yl)azo)-5-nitrobenzenesulfonic acid-monosodium salt (CI15685; Acid Red No. 184), (2-sulfophenyl)di[4-(ethyl((4-sulfophenyl)methyl)amino)phenyl]-carbenium-disodium salt betaine (CI42090; Acid Blue No. 9; FD&C Blue No. 1), 1,4-bis[(2-sulfo-4-methylphenyl)amino]-9,10-anthraquinone-disodium salt (CI 61570; Acid Green No. 25), bis[4-(dimethylamino)phenyl]-(3,7-disulfo-2-hydroxynaphth-1-yl)carbenium-internal salt monosodium salt (CI44090; Food Green No. 4; Acid Green No. 50), bis[4-(diethylamino)phenyl](2,4-disulfophenyl)carbenium-internal salt, sodium salt (2:1) (CI42045; Food Blue No. 3; Acid Blue No. 1), bis[4-(diethylamino)phenyl](5-hydroxy-2,4-disulfophenyl)carbenium-internal salt, calcium salt (2:1) (CI42051; Acid Blue No. 3), 1-amino-4-(cyclohexylamino)-9,10-anthraquinone-2-sulfonic acid-sodium salt (CI62045; Acid Blue No. 62), 1-amino-4-(phenylamino)-9,10-anthraquinone-2-sulfonic acid (CI62055; Acid Blue No. 25), 2-(1,3-dihydro-3-oxo-5-sulfo-2H-indol-2-yliden)-2,3-dihydro-3-oxo-1H-indol-5-sulfonic acid-disodium salt (CI73015; Acid Blue No. 74), 9-(2-Carboxyphenyl)-3-[(2-methylphenyl)amino]-6-[(2-methyl-4-sulfo-phenyl)amino]xanthylum-internal salt, monosodium salt (CI45190; Acid Violet No. 9), 1-hydroxy-4-[(4-methyl-2-sulfophenyl)amino]-9,10-anthraquinone-sodium salt (CI60730; D&C Violet No. 2; Acid Violet No. 43), bis[3-nitro-4-[(4-

phenylamino)-3-sulfo-phenylamino]-phenyl]-sulfone (CI10410; Acid Brown No. 13), 5-amino-4-hydroxy-6-[(4-nitrophenyl)azo]-3-(phenylazo)-2,7-naphthaline-disulfonic acid disodium salt (CI20470; Acid Black No. 1), 3-hydroxy-4-[(2-hydroxynaphth-1-yl)azo]-7-nitro-1-naphthaline-sulfonic acid-chromium complex (3:2) (CI15711; Acid Black No. 52), 3-[(2,4-dimethyl-5-sulfophenyl)azo]-4-hydroxy-1-naphthaline-sulfonic acid-disodium salt (CI14700; Food Red No. 1; Ponceau SX; FD&C Red No. 4), 4-(acetylamino)-5-hydroxy-6-[(7-sulfo-4-[(4-sulfophenyl)azo]naphth-1-yl)azo]-1,7-naphthaline-disulfonic acid-tetrasodium salt (CI28440; Food Black No. 1), 3-hydroxy-4-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-ylazo)-naphthaline-1-sulfonic acid-sodium salt, chromium complex (Acid Red No. 195).

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Further colorants known for the purpose of hair coloration, which may be contained in the coloring composition in accordance with the present invention are disclosed in E. Sagarin, "Cosmetics, Science and Technology", Interscience Publishers Inc., New York (1957), page 503 and onwards, as well as H. Janistyn, "Handbuch der Kosmetika und Riechstoffe", Volume 3 (1973), page 388 and onwards and K. Schrader, "Grundlagen und Rezepturen der Kosmetika", 2nd Edition (1989), pages 782-815.

25

Suitable hair coloring pigments are substantially insoluble colorants in the medium employed in the composition of the present invention and these pigments may be inorganic or organic. Inorganic-organic mixed pigments are also suitable.

- 5 The pigments are preferably not nanopigments. The preferred particle size is from 1 to 200  $\mu\text{m}$ , preferably 3 to 150  $\mu\text{m}$ , more preferably 10 to 100  $\mu\text{m}$ . Preferred are inorganic pigments. The inorganic pigments may be of natural origin, and may for example be prepared from chalk, ochre, umbra, green earth,
- 10 burnt terra di sienna or graphite. The pigments may be white pigments, such as titanium dioxide or zinc oxide, they may be black pigments, such as iron oxide black, they may be colored pigments, such as ultra marine or iron oxide red, they may be gloss pigments, metallic effect pigments, pearlescent pigments
- 15 as well as fluorescent or phosphorescent pigments, although preferably at least one pigment is a colored pigment, i.e. a non-white pigment. Suitable are metal oxides, metal hydroxides and metal oxide hydrates, mixed phase pigments, sulphur - containing silicates, metal sulphides, complex metal cyanide s,
- 20 metal sulphates, metal chromates and metal molybdates as well as the metals themselves (bronze pigments). Suitable are in particular titanium dioxide (CI 77891), black iron oxide (CI 77499), yellow iron oxide (CI 77492), red and brown iron oxide (CI 77491), manganese violet (CI 77742), ultramarine (sodium -
- 25 aluminium sulfosilicates, CI 77007, pigment blue 2), chromium oxide hydrate (CI 77289), iron blue (ferric ferrocyanide, CI

77510), carmine (cochineal). In particular preferred are pigments on the basis of mica or laminated silica minerals which are coated with a metal oxide or a metal oxychloride, such as titanium dioxide or bismuth oxychloride, as well as 5 additional coloring components, such as iron oxides, iron blue, ultramarine, carmine, etc., where in the color is determined by means of the variation of the layer thickness. Such pigments are for example sold under the trade names Rona®, Colorona®, Dichrona® and Timiron® of the Company Merck, Germany. Organic 10 pigments are for example the natural pigments sepia, gummigutt, bone coal, cassel brown, indigo, chlorophyll and other plant pigments. Synthetic organic pigments are for example azo pigments, anthraquinoid pigments, indigoid pigments, dioxazine pigments, chinacridone pigments, pthalocyanine pigments, 15 isoindolinone pigments, perylene pigments, perinone pigments, metal complex pigments, alkali blue pigments and diketopyrrolopyrrol pigments.

The hair treatment composition in accordance with the present 20 invention preferably comprises additionally at least one hair cosmetic in an amount of from 0.01 to 10, more preferably of from 0.05 to 5 weight %. Preferred hair cosmetics are silicone compounds as well as cationic compounds, which possess due to cationic groups or groups which can be rendered cationic, in 25 particular primary, secondary, tertiary or quaternary amine groups, a substantivity to human hair. Suitable cationic

compounds are selected among cationic surfactants, betainic, amphoteric surfactants, cationic polymers, silicone compounds having a cationic group or groups which can be rendered cationic, cationic derivatized proteins or protein hydrolyzates

5 and betain.

Suitable silicone compounds are for example polydimethylsiloxane (INCI: Dimethicone),  $\alpha$ -hydro- $\omega$ -hydroxypolyoxydimethylsilylene (INCI: Dimethiconol), cyclic 10 dimethylpolysiloxane (INCI: cyclomethicone), trimethyl(octadecyloxy)silane (INCI: stearoxytrimethylsilane), dimethylsiloxane/glycol copolymer (INCI: dimethicone copolyol), dimethylsiloxane/aminoalkylsiloxane copolymer having terminal 15 hydroxy groups (INCI: amodimethicone), monomethylpolysiloxane having lauryl side chains and terminal polyoxyethylene chains and/or polyoxypropylene chains (INCI: lauryl methicone copolyol), dimethylsiloxane/glycol copolymer acetate (INCI: dimethiconcopolyol acetate), dimethylsiloxane/aminoalkylsiloxane copolymer having terminal 20 trimethylsilyl groups (INCI: trimethylsilylamodimethicone).

Preferred silicone polymers are dimethicone, cyclomethicone and dimethiconole. Mixtures of silicone polymers are also suitable, for example a mixture of dimethicone and dimethiconol. The designations provided in brackets correspond 25 to the nomenclature in accordance with INCI (International

Cosmetic Ingredients), which is employed for the designation of cosmetically relative active ingredients and additives.

Usually further known cosmetic additives may be added to the  
5 hair treatment composition in accordance with the present invention, for example non-fixative non-ionic polymers, such as polyethylene glycols, non -fixative, anionic and natural polymers as well as mixtures thereof, in amounts of preferably from 0.01 to 50 weight %. Perfume oils in amount of from 0.01  
10 to 5 weight %, opacifier such as ethyleneglycoldistearate in an amount of from 0.01 to 5 weight %, surfactants or emulsifiers selected from the classes of anionic, cationic, amphoteric or non-ionic surfactants, such as fatty alcohol sulfates, ethoxylated fatty alcohols, fatty acid alkanolamides, such as  
15 esters of hydrated fatty acids from rizinus oil, in an amount of from 0.1 to 30 weight %, as well as moisturizers, dye receptivity improving agents, light protective agents, anti - oxidative agents as well as preservatives in amounts of from 0.01 to 10 weight % may be added.

20

Figure 1 shows schematically the method for the provision of a recallable, permanent hairdo. A strand of hair is wound onto a curler (bobbin) and a solution in accordance with the present invention comprising a cross -linkable macromer is sprayed  
25 thereon. By irradiation with a suitable source of energy, for

example a UV lamp, the desired permanent shade is fixed.

Subsequently the curler is removed.

Figure 2 shows the deformation of a permanent hairdo and the  
5 recovery of the permanent shape starting from the temporary  
shape. The hair curl in the permanent shape possesses a length  
 $l_0$ . The curl in the deformed shape has a length  $l_1$ . The curl  
in the recovered shape has a length  $l_2$ . The degree of re -  
attaining the permanent shape (recovery) can be calculated as  
10 follows: Recovery =  $(l_1 - l_2) / (l_1 - l_0)$ .

As measure for the evaluation of the shape memory property of a  
composition the memory factor may be employed, which considers  
the transformation ability of a permanent hairdo into a  
15 temporary sha pe (shaping factor) as well as the recovery  
attainability of the permanent form starting from the temporary  
form (recovery factor, degree of recovery). If one starts with  
the consideration from an even strand of hair onto which a  
curly shape has been impr essed as permanent shape and onto  
20 which, subsequently, a second, even shape has been impressed as  
temporary shape, the shaping factor can be determined in  
accordance with the following criterion:

Degree of evenness	Shaping factor
Strong curl from the hairline to the end of hair	0
Lesser degree of curliness from the hairline to the end of hair	1
Hairline even, end of hair in the form of a curl	2
Hairline even, slight curvature at the end of hair	3
Even from the end of hairline to the end of hair	4

The recovery factor can be determined in accordance with the following criterion:

Degree of recovery of the permanent shape	Recovery factor
0%	0
30%	1
40%	2
50%	3
60%	4
75%	5
100%	6

5

The memory factor  $M$  can be calculated using the shaping factor  $F$ , the maximum shaping factor  $F=4$ , the recovery factor  $r$  and the maximum recovery factor  $R=6$  in accordance with the following equation

$$M = (f/F) * (r/R) * 100$$

The memory factor should ideally be not below 25, preferably the factor should be between 25 and 33.3, more preferred 5 between 37 and 100.

The following examples are intended to illustrate the subject matter of the present invention further.

10

### Examples

**Example 1: Hair treatment using a thermoset shape memory polymer**

	A
Poly( $\epsilon$ -caprolactone dimethacrylate <sup>1</sup> )	2 g
THF	Ad 100 g

1) Prepared in accordance with Example 2 of WO 99/42147

15 Onto even hair strands having each a length of 19 cm approximately 1 g of the composition are applied. The strands are wound on curlers and dried. Subsequently the strands are warmed to about 65 to 70°C and a photochemical cross -linking reaction is carried out (UV light, Hg -lamp). After cross - 20 linking and cooling to room temperature the curlers are removed. The curls (impressed permanent shape) had a length of 8 cm.

In order to simulate a deformation by means of cold shaping the  
curls were subjected to a load of 25 g and were let to hang at  
room temperature for a) 1 hour, b) 2 hours and 3) 3 hours. The  
length of the curls after deformation were a) 10 cm, b) 10 cm  
5 and c) 11.2 cm.

After removal of the weights the strands were heated to about  
65 to 70°C. The curls retracted spontaneously to lengths of a)  
8 cm, b) 8 cm and c) 8.3 cm. This corresponds to a degree of  
10 recovery of the impressed hairdo of a) 100%, b) 100% and c )  
91%. The degree of recovery (Recovery) can be calculated (see  
Figure 2) as follows:

$$\text{Recovery} = (l_1 - l_2) / (l_1 - l_0)$$

15

In order to impress a second hairdo (temporary shape) a wavy  
strand (curl) of a length of 3.2 cm was warmed to 70°C and  
stretched to the initial, complete length of 6.3 cm.  
Subsequently the strand was cooled. Upon heating to about 65  
20 to 70°C the curl spontaneously retracted to a length of 3.9 cm.  
This corresponds to a degree of recovery of the impressed  
hairdo (shape) of 77%.

**Examples 2 to 31: Hair treatment using a shape memory polymer**

25

Compositions were prepared comprising each 2 weight % macromer in a mixture of ethanol and water (50/50) employing the following macromers and macromer mixtures in the indicated weight ratios.

5

	2	3	4	5	6	7	8	9
PEG (4k) - DMA	100	100						
PEG (8k) - DMA			100	100	70	70	80	80
PPG- (475) - MA					30	30	20	20
initiator	-	AiBN	-	AiBN	-	AiBN	-	AiBN

	10	11	12	13	14	15	16	17
PEG (8k) - DMA	70	70	80	80	70	70	80	80
PEG- (526) - MA	30	30	20	20				
PPG- (430) - MA					30	30	20	20
initiator	-	AiBN	-	AiBN	-	AiBN	-	AiBN

	18	19	20	21	22	23	24	25
PEG(8k) - DMA	70	70	80	80	70	70	80	80
NoO- PPG(400) - MA	30	30	20	20				
MeO- PEG(300) - MA					30	30	20	20
initiator	-	AiBN	-	AiBN	-	AiBN	-	AiBN

	26	27	28	29	30	31
PEG(8k) - DMA	70	70	80	80		
MeO- PPG(200) - MA	30	30	20	20		
PEG(10k) - DMA					100	100
Initiator	-	AiBN	-	AiBN	-	AiBN

Application of compositions 2 to 31 was carried out as

5 explained in Example 1. The results obtained were comparable.

**Examples 32 to 41: Hair treatment using shape memory polymers**

Compositions were prepared comprising each 2 weight % macromer in THF using the following macromers and macromer mixtures in

5 the weight ratios as indicated:

	32	33	34	35	36	37	38	39	40	41
PLGA(7k) - DMA	100	100								
PCl(10k) - DMA			100	100	70	70	70	70	70	70
NoO- PPG(400) - MA					30	30				
NoO- PPG(475) - MA							30	30		
PEG(526) - MA									30	30
initiator	-	AiBN	-	AiBN	-	AiBN	-	AiBN	-	AiBN

The application of compositions 32 to 41 was carried out as disclosed in Example 1. The results obtained were comparable.

**Example 42: Hair treatment using shape memory polymer**

A composition was prepared comprising 2 weight % PLGA(7k) -DMA macromer in ethylacetate and this composition was applied on hair. After the hair has been brought into the desired shape this shape was fixed by means of irradiation with UV light.

5

The preparation of the macromers employed in Examples 2 to 42 was carried out on the basis of the disclosure in WO 99/42147.

10 The abbreviations as used in the examples to designate the following materials:

PEG(4k)-DMA, PEG(8k)-DMA, PEG(10k)-DMA: poly(ethylene-glycol)-dimethacrylate

PPG-(475)-MA, PPG-(430)-MA: poly(propylene-glycol)-methacrylate

15 PEG-(526)-MA poly(ethylene-glycol)-methacrylate

NoO-PPG(400-MA, NoO-PPG(475)-MA: nonyl-poly(propylene-glycol)-methacrylate

MeO-PEG-(300)-MA: methyl-poly(ethylene-glycol)-methacrylate

MeO-PPG(200)-MA: methyl-poly(propylene-glycol)-methacrylate

20 PLGA(7k)-DMA: poly(L-lactide-co-glycolide)-dimethacrylate

PC1(10k)-DMA: poly( $\epsilon$ -caprolactone)-dimethacrylate

**Examples 43-50: hair treatment using thermoplastic shape memory polymers**

25

The shape memory polymers used in the following were prepared from two different macrodiols and trimethylhexan

-1,6-

diisocyanate in accordance with the procedure disclosed in example 1 of WO 99/42147. Compositions for hair treatment were prepared comprising 0.5 wt.-% of the multiblock copolymer in a suitable solvent or solvent mixture, such as water, ethanol, 5 tetrahydrofuran, trichloromethane or a mixture of water/ethanol/THF.

Macrodiol	43	44	45	46
PDX 1500 [wt.-%]	48			
PLGA 2000 [wt.-%]	52			
PCL 4000 [wt.-%]		60		
PCL 10000 [wt.-%]			50	60
PDL 2000 [wt.-%]		40		
PDL 3000 [wt.-%]			50	40
$M_w$ Copolymer [g/mol]	79100	150000	130000	115000
$T_{trans}$ [°C]	34	48	55	55
$T'_{trans}$ [°C]	85	89	87	87

10

Macrodiol	47	48	49	50
PCL 10000 [wt.-%]	78	59	40	20
PDL 10000 [wt.-%]	22	41	60	80
$M_w$ Copolymer [g/mol]	208000	357000	282000	300100
$T_{trans}$ [°C]	55	54	55	54
$T'_{trans}$ [°C]	91	91	93	94

The abbreviations of the macrodiols have the following meaning:

PDX: Poly(para-dioxanone)

PLGA: Poly(L-lactide-co-glycolide)

PCL: Poly( $\epsilon$ -caprolactone)

15 PDL: Poly(pentadecalactone)

The numbers presented in connection with the macrodiols represent the approx. molecular weight of the macrodiols ( $\pm$  100).

- 5 7 g of the composition is applied onto even hair strands. The hair is wound onto curlers, followed by drying. Subsequently the hair is warmed to about 95°C. After cooling to room temperature (about 25°C) the curlers are removed. The curls (impressed permanent shape) had a length of 4.5 cm. Impressing
- 10 a second shape of a hairdo (temporary shape) is achieved by warming the curled strand to about 55°C, stretching the hair to the initial full length (16 cm) and cooling to room temperature. Rewarming to about 55°C gave rise to a spontaneous retraction of the curls to a length of 8 cm. This corresponds
- 15 to a degree of recovery of about 70%.